Deformation of Microporous Carbon during Adsorption of Nitrogen, Argon, Carbon Dioxide, and Water Studied by in Situ Dilatometry

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ABSTRACT: Adsorption-induced deformation of a monolithic, synthetic carbon of clearly distinguishable micro- and mesoporosity was analyzed by in situ dilatometry with N₂ (77 K), Ar (77 K), CO₂ (273 K), and H₂O (298 K). A characteristic nonmonotonic shape of the strain isotherm showing contraction of the sample at initial micropore adsorption followed by expansion toward completion of micropore filling was found for all adsorbates. However, the extent of contraction and expansion varied significantly with the adsorbate type. The deformation differences observed were compared with the density ratio of the adsorbates within the micropores and the respective unconfined fluids. In particular, CO₂ caused the least contraction of the sample, while in parallel adsorbed CO₂ molecules were predicted to be considerably compacted inside carbon micropores compared to bulk liquid CO₂. On the contrary, the packing of H₂O molecules within carbon micropores is less dense than in the bulk liquid and adsorption of H₂O produced the most pronounced contraction. N₂ and Ar, both exhibiting essentially the same densities in adsorbed and bulk liquid phase, induced very similar deformation of the sample. These findings support theoretical predictions, which correlate adsorption-induced deformation and packing of molecules adsorbed in micropores. Additionally for the first time, we demonstrated with the N₂ strain isotherm the existence of two nonmonotonic stages of subsequent contraction and expansion in the regions of micropore and mesopore filling. This characteristic behavior is expected for any micro- and mesoporous material.

1. INTRODUCTION

The effect of adsorption-induced deformation, i.e., the structural change of an adsorbent during the adsorption of molecules or ions, has been scientifically investigated since the beginning of the past century¹² and is considered an intrinsic part of the adsorption process. For most nanoporous materials, the reported adsorption-induced deformation does not exceed the order of 1% and is therefore neglected in most technical applications. Exceptions are metal–organic frameworks³ and silica aerogels,⁴ where the deformation was shown to reach tens of percent. However, even for small deformations, the related stresses may mount up to thousands of atmospheres and compromise the adsorbent integrity. A characteristic example for this is the deformation of coal upon CO₂ adsorption during CO₂ storage in geological formations or enhanced coal bed methane recovery, e.g., refs ⁵ and ⁶. With respect to fundamental research, adsorption-induced deformation has been attracting considerable interest in recent years: various theoretical approaches were applied to predict adsorption stress in nanopores and its effect on the solid porous matrix as well as the confined fluid, e.g., refs ⁷–⁶²; in addition, experimental results related to adsorption-induced deformation were shown to allow for mechanical characterization of nanoporous matrices and their solid backbones, respectively, e.g., refs ⁴ and ⁶⁸–⁶⁰.

Adsorption-induced deformation of microporous materials (coals, synthetic carbons, activated carbons, zeolites) in particular was experimentally studied with various gases, e.g., refs ¹ and ³⁰–⁴⁹. While it is commonly expected that adsorption should induce expansion of the porous matrix, the majority of investigated microporous adsorbents exhibited nonmonotonic deformation with contraction at low pressures followed by expansion as adsorption progresses. In 1930, Bangham and Fakhoury proposed a thermodynamic model to describe the expansion of coal based on the reduction of the interfacial energy of solid and adsorbate;⁵⁰ however, by its nature this model cannot explain the experimentally detected contraction of microporous materials. In 1957, Lakhanpal and Flood suggested that the contraction of coals might result from molecular “bridging” between high-energy sites within micropores.⁴⁰ In 1980, grand canonical Monte Carlo simulations predicted the pressure of the adsorbed phase inside a micropore (often referred to as solution pressure or adsorption stress) to

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become positive or negative depending on the size of the pore and the adsorptive molecule, respectively. 1,52 This correlation between pore size and solvation pressure was later interpreted as an effect of molecular packing, i.e., dense layering inside the pores causes positive solvation pressure, while loose packing gives rise to negative solvation pressure (see e.g. ref 53). In 2006, Ravikovitch and Neimark linked the concept of solvation to the phenomenon of adsorption-induced deformation of micropores, suggesting a rigorous theoretical interpretation of the physical mechanisms of the nonmonotonic deformation behavior in micropores. 5 Using density functional theory, the authors demonstrated that the deformation could be explained by a competition between adsorbate–adsorbent attraction at low density of adsorbed molecules and repulsion due to packing effects at higher density. As such, a negative solvation pressure in a micropore could be understood as a mediation of the attractive pore wall potentials by adsorbed molecules, while on the other hand, a positive solvation pressure should result from high fluid densities inside the micropore, when the short-range repulsive interactions between fluid–fluid and fluid–solid molecules become more significant. Since then, several authors applied molecular simulations to model the adsorption-induced deformation of micropores at experimental conditions, 9,10,12–14,18–21,54,55 in some cases achieving reasonable agreement with experimental data. In this context, the nonmonotonic deformation of microporous carbons was interpreted as a result of a broad pore size distribution within the material leading to a net deformation, which is a superposition of micropores exhibiting positive and negative solvation pressure, respectively.10 Investigating the phenomenon of adsorption-induced deformation with respect to different adsorbates earlier studies revealed a significant correlation between adsorbate applied and deformation observed. 31,34,39–42 However, comparing these studies with the current theoretical understanding of adsorption-induced deformation is hardly feasible due to insufficient data. The adsorption isotherms corresponding to the observed deformations were reported only in few cases, and structural characterization of the samples in terms of micropore size, surface area, etc., was often very limited, if given at all. Also, the gases used for deformation measurements often included various alcohols and hydrocarbons with substantial differences in molecular size, which might have distinct micropore accessibility. Here, we applied the in situ dilatometry technique we introduced in ref 30 which allows exploring the adsorption deformation phenomenon as a coupled process under controlled conditions. We simultaneously measured in one apparatus the adsorption isotherm and the corresponding one-dimensional deformation of a microporous carbon using the adsorbates N2 (77 K), Ar (77 K), CO2 (273 K), and H2O (298 K). Complementary we performed a thorough structural characterization of the sample investigated. This approach permits to draw unambiguous conclusions about the effects of pore structure and phase behavior of adsorbed gases on the deformation of microporous adsorbents.

2. EXPERIMENTAL SECTION

2.1. Sample Synthesis and Structural Characterization. The sample investigated was a cylindrical monolithic rod of synthetic microporous carbon of length L0 = 58.6 mm and diameter 3.3 mm prepared in our lab. The underlying sol–gel based synthesis of the organic precursor followed the protocol given in ref 56. The molar ratio of resorcinol and formaldehyde to the mass of the total starting solution was 50%. The organic precursor of the sample was dried under ambient conditions and carbonized in argon atmosphere at a temperature of 800 °C.

The electrically conductive sample was investigated by scanning electron microscopy (SEM) operating at 5 kV without further sample preparation such as sputter coating. Furthermore, adsorption isotherms for N2 at 77 K, Ar at 77 K, and CO2 at 273 K were obtained by a commercial volumetric adsorption instrument (ASAP 2020 Micromeritics, Norcross, GA) during the in situ dilatometry experiments (for details see section 2.2).

2.2. In Situ Dilatometry Measurements. The experimental setup for in situ dilatometry consists of a commercial volumetric adsorption instrument (ASAP 2020 Micromeritics, Norcross, GA) equipped with a self-designed dilatometer. The essential parts of the dilatometer are a linear variable differential transducer (LVDT; Macro Sensors, Pennsauken, NJ) and a custom-built sample holder. A more detailed description of the setup is given in ref 30. The overall setup simultaneously yields the specific amount adsorbed and the length change of the sample L at the corresponding relative gas pressure p/p0. Prior to each measurement, the sample was degassed in the sample holder attached to the analysis port of the adsorption instrument for at least 1 day at a temperature of 300 °C and a pressure below 10−3 mbar. This way the sample had no contact with ambient atmosphere between degassing and the actual measurement. From the obtained dilatometric data we calculated the relative length change ΔL/(L−L0) with ΔL the change of the sample length with respect to its evacuated and degassed state prior to the adsorption measurement and L0 the length of the degassed sample rod. Thus, the regular adsorption isotherm is complemented by the deformation or strain isotherm ΔL/(L−L0). The accuracy of ΔL is approximately ±0.2 μm, resulting in a resolution of ΔL/L0 of approximately ±5 × 10−6 for the sample investigated. The adsorbates used were of the following purities: 5.0 for N2, 5.0 for Ar, and 4.5 for CO2. For H2O adsorption measurements the instrument was equipped with a vapor option upgrade provided by the instrument’s producer filled with ultrapure water prepared according to ISO 3696:1987 (grade 1). To additionally remove CO2 dissolved in the water, the liquid filled tank was slowly frozen from bottom to top, and subsequently the headspace above the ice was evacuated. To control the sample temperature, the sample holder was placed in a liquid N2 bath of approximately ±77 K for N2 and Ar adsorption measurements, and the respective saturation pressures p0 were directly measured at regular intervals by the instrument. For CO2 and H2O adsorption measurements a liquid bath was used. The bath temperature was measured with an external platinum temperature sensor (accuracy ±0.2 K) and maintained by means of a thermostat. The saturation pressures for CO2 and H2O at their respective measurement temperatures of 273 and 298 K were taken from the literature. 57 The maximal absolute gas pressure possible within the commercial adsorption instrument was approximately 1 bar; therefore, the CO2 experiment was limited to relative pressures <0.03.

3. RESULTS AND DISCUSSION

3.1. Sample Characterization. A SEM image of the carbon sample investigated is given in Figure 1 showing a disordered network consisting of approximately spherical interconnected particles of diameter d50 in the range of 15–30 nm. A comprehensive study of the microstructure of this class of carbon material was recently published in ref 58. As will be discussed further below, the interparticle pore network of the sample is entirely within the range of mesoporous, while the intraparticle porosity is exclusively microporous. With respect to in situ dilatometry it is important to note that the interparticle pore network and the intraparticle structure are entirely isotropic and disordered; thus, the absence of a predominant direction results in an isotropic adsorption-induced deformation of the sample. The mass and the spatial dimensions of the carbon rod were determined after 1 day of...
degassing at a temperature of 300 °C and a gas pressure below 10⁻² mbar. The sample volume was calculated from the geometric dimensions of the cylindrical sample yielding a macroscopic (apparent) density \( \rho_{\text{app}} = 0.741 \pm 0.016 \, \text{g/cm}^3 \).

The characterization of the pore structure was performed on the base of the adsorption isotherms (N\(_2\) (77 K), Ar (77 K), and CO\(_2\) (273 K)) determined in the in situ dilatometry experiments (see Figures 3 and 4a). The N\(_2\) adsorption isotherm in Figure 3a has a shape typical for materials with clearly separated regimes of micro- and mesopores. From the N\(_2\) adsorption isotherm the specific external surface area \( S_{\text{ext}} = 205 \pm 10 \, \text{m}^2/\text{g} \), i.e., the envelope area of the particle network, and the specific micropore volume \( V_{\text{mic}} = 0.20 \pm 0.01 \, \text{cm}^3/\text{g} \) was determined applying the t-plot method using the reference adsorption isotherm suggested by Magee for carbon black. Furthermore, the total specific pore volume \( V_{\text{tot}} = 0.86 \pm 0.01 \, \text{cm}^3/\text{g} \) was calculated according to the Gurvich rule at a relative pressure of approximately 0.99. Combining the macroscopic density \( \rho_{\text{app}} \), the total specific pore volume \( V_{\text{tot}} \) and the specific micropore volume \( V_{\text{mic}} \) the density of the nonporous carbon phase \( \rho_c \) and the particle density \( \rho_{\text{part}} \) were derived by \( \rho_{\text{c}}(N_2) = 1/(1/\rho_{\text{m}} - V_{\text{mic}}) = 2.05 \pm 0.13 \, \text{g/cm}^3 \) and \( \rho_{\text{part}} = 1/(1/\rho_{\text{c}} - (V_{\text{tot}} - V_{\text{mic}})) = 1.45 \pm 0.07 \, \text{g/cm}^3 \), respectively. The carbon density \( \rho_{\text{c}}(N_2) \) is well in line with numerical values determined by He pycnometry (\( \rho_{\text{c}}(\text{He}) = 2.06 \pm 0.06 \, \text{g/cm}^3 \)) and dynamic gas expansion (DGE) (\( \rho_{\text{c}}(\text{DGE}) = 2.190 \pm 0.125 \, \text{g/cm}^3 \)) measurements reported for carbons prepared according to very similar protocols. Therefore, we conclude that all the porosity of sample is accessed by N\(_2\) adsorption; i.e., there is no steric or diffusive restriction for N\(_2\) entering the microporosity, and all porosity of the sample is entirely within the range of micro- and mesopores. For the calculation of the particle density \( \rho_{\text{part}} \) the intraparticle porosity is considered exclusively microporous. This assumption is supported by the experimental finding that sol–gel based carbons can be synthesized as macroporous particle networks using the same protocol but slightly different educt concentrations. These macroporous carbons exhibit approximately the same specific micropore volume as the sample investigated but no mesoporosity.

For an investigation of the sample’s pore size distribution (PSD) nonlocal and quenched solid density functional theory (NLDFT and QSDFT) were applied. The N\(_2\) (77 K) adsorption isotherm was analyzed by a QSDFT hybrid kernel of slit-shaped carbon micropores and cylindrical carbon mesopores. As can be seen from the respective cumulative and differential PSDs shown in Figure 2a, the sample exhibits a broad mesopore size distribution with a maximum at an average mesopore diameter \( d_{\text{meso}} \approx 18 \, \text{nm} \).

The micropore structure was further analyzed using the adsorption isotherms of N\(_2\) (77 K), Ar (77 K), and CO\(_2\) (273 K) and the NLDFT models for carbon slit-shaped micropores described in refs 65. Respective cumulative and differential micropore volume distributions are shown in Figure 2b. With respect to the lower end of the PSD it was pointed out in ref 65 that—due to the experimental pressure resolution of currently available commercial instruments—the reliability of micropore size distributions calculated from N\(_2\) and Ar adsorption data taken at 77 K is limited to pore widths above approximately 0.5 nm. Thus, we assume the NLDFT results derived from CO\(_2\) adsorption data to be the most reliable at the lower end of the pore size distribution. Overall, the micropore size distribution of the sample is also rather wide exhibiting the majority of pore volume in the range of 0.35–0.8 nm.

All structural parameters derived are summarized in Table 1.

3.2. In Situ Dilatometry. The experimental adsorption isotherms and the corresponding in situ dilatometry data are shown for N\(_2\) (77 K) and Ar (77 K) in Figure 3 and for CO\(_2\) (273 K) and H\(_2\)O (298 K) in Figure 4. All adsorption isotherms are given in units of free liquid volume; the respective liquid densities of the adsorbates are given in Table 2. For CO\(_2\) and H\(_2\)O the desorption branches of adsorption and strain isotherms are included, while for N\(_2\) and Ar desorption data could not be obtained in the relative pressure range of micropore filling due to the very slow desorption kinetics at 77 K. The often reported nonmonotonic deformation during carbon micropore filling was found for all adsorbates; i.e., the sample contracts at the beginning of micropore filling crossing over to expansion with further increasing relative pressure, though in the case of our...
Table 1. Structural Parameters of the Carbon Sample Investigated\textsuperscript{44}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_m ) [g/cm(^3)]</td>
<td>0.741 ± 0.016</td>
</tr>
<tr>
<td>( \rho_{\text{tot}} ) [g/cm(^3)]</td>
<td>1.45 ± 0.07</td>
</tr>
<tr>
<td>( \rho_c(N_2) ) [g/cm(^3)]</td>
<td>2.05 ± 0.13</td>
</tr>
<tr>
<td>( V_m ) [cm(^3)/g]</td>
<td>0.86 ± 0.01</td>
</tr>
<tr>
<td>( V_{\text{tot}} ) [cm(^3)/g]</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>( S_{\text{ext}} ) [m(^2)/g]</td>
<td>205 ± 10</td>
</tr>
<tr>
<td>( d_{\text{meso}} ) [nm]</td>
<td>18</td>
</tr>
<tr>
<td>( d_{\text{part}} ) [nm]</td>
<td>15–30</td>
</tr>
</tbody>
</table>

\( \rho_m, \rho_{\text{tot}}, \) and \( \rho_c(N_2) \) are the densities of the macroscopic sample rod, the spherical particles seen in Figure 1, and the nonporous carbon phase as derived from \( N_2 \) sorption data, respectively. \( V_m \) and \( V_{\text{tot}} \) are the specific total pore volume and micropore volume, respectively. \( S_{\text{ext}} \) is the specific external surface area, i.e., the envelope surface area of the particles. \( d_{\text{meso}} \) is the average mesopore diameter and \( d_{\text{part}} \) the range of particle diameters as seen by SEM.

For the discussion of the experimental results, we first directly compare the data for the adsorption of \( N_2 \) and Ar at 77 K over the whole relative pressure range up to saturation (Figure 3a). Here the most striking difference is the lack of mesopore filling (i.e., capillary condensation/evaporation) in the case of Ar, which is clearly visible in the \( N_2 \) adsorption isotherm as a hysteresis loop in the relative pressure range between 0.8 and 0.95. It is known\textsuperscript{66} that the measurement temperature of 77 K—being 6.5 K below the triple point of free argon—prevents capillary condensation of Ar in pores larger than approximately 12 nm, which basically includes the entire mesoporosity present in our sample (compare pore size distribution in Figure 2a). Nevertheless, the corresponding strain isotherms when plotted on a linear scale are virtually identical for \( N_2 \) and Ar; only minor adsorption-induced deformation due to capillary effects is evident in the case of \( N_2 \) adsorption (see inset in Figure 3a). This leads to the conclusion that the adsorption-induced deformation of our sample essentially arises from adsorption in micropores and on the enveloping area of the particle network. It should be noted that the minor deformation for filled mesopores is the consequence of the rather high macroscopic density of the sample (\( \rho_m = 0.741 ± 0.016 \) g/cm\(^3\)) and the accompanying high bulk modulus, which diminish deformation related to mesopore filling. A more detailed description of adsorption-induced deformation of mesoporous materials and its respective mechanisms is e.g. given in refs 4 and 11. Taking a look at the adsorption and strain isotherms in the relative pressure range of micropore filling (Figure 3b), we find the experimental results not only qualitatively but also quantitatively very similar except for a shift in relative pressure. This shift can be attributed to the enhanced solid–fluid interaction energy of \( N_2 \) due to its quadrupole moment.\textsuperscript{67} The result that the adsorption of \( N_2 \) and Ar adsorption lead to very similar deformation was also found in ref 39 for a coal sample at 25 °C.

Table 2. Summary of Physical Properties for the Adsorbates \( N_2, \) Ar, \( CO_2, \) and \( H_2O \)\textsuperscript{44}

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>( d_{\text{mol}} ) [nm]</th>
<th>( m_{\text{ads}} ) [g/mol]</th>
<th>( V_{\text{mol}} ) [cm(^3)/mol]</th>
<th>( \rho_{\text{ads}} ) [g/cm(^3)]</th>
<th>( \rho_{\text{liquid}} ) [g/cm(^3)]</th>
<th>( p_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 )</td>
<td>0.36</td>
<td>28.01</td>
<td>34</td>
<td>0.84</td>
<td>0.807</td>
<td>1.04</td>
</tr>
<tr>
<td>( Ar )</td>
<td>0.34</td>
<td>39.95</td>
<td>28</td>
<td>1.43</td>
<td>1.396</td>
<td>1.02</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>0.33</td>
<td>44.01</td>
<td>38</td>
<td>1.15</td>
<td>0.927</td>
<td>1.24</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>0.27</td>
<td>18.02</td>
<td>23</td>
<td>0.78</td>
<td>0.997</td>
<td>0.78</td>
</tr>
</tbody>
</table>

\( d_{\text{mol}} \) is the kinetic molecular diameter,\textsuperscript{66} \( m_{\text{ads}} \) the molar mass,\textsuperscript{67} \( \rho_{\text{mol}} \) the density of the free bulk liquid,\textsuperscript{57} \( V_{\text{mol}} \) the molar volume of the adsorbate, \( \rho_{\text{ads}} = m_{\text{ads}}/V_{\text{mol}} \) the respective density of the adsorbate, and \( p_f = \rho_{\text{ads}}/\rho_{\text{liquid}} \) the ratio of adsorbate to free liquid density. The densities of the free liquids correspond to saturation pressure and 77 K for \( N_2, \) 87 K for Ar, 273 K for \( CO_2, \) and 298 K for \( H_2O. \) For \( N_2, \) Ar, and \( CO_2 \), \( V_{\text{mol}} \) was taken from NLDFT calculations,\textsuperscript{44} while for \( H_2O \) \( \rho_{\text{ads}} \) was derived from experimental data and \( V_{\text{mol}} \) was calculated according to \( V_{\text{mol}} = m_{\text{ads}}/\rho_{\text{ads}}. \)

Figure 3. Results of the \textit{in situ} dilatometry measurement for the adsorption of \( N_2 \) (77 K) and Ar (77 K) on the carbon sample. Upper panels: sorption isotherms; lower panels: corresponding strain isotherms. Full symbols denote adsorption and open symbols desorption. (a) Experimental results over the entire pressure range up to saturation. The inset in the lower panel is a magnification of the sample’s deformation in the relative pressure range of capillary condensation for \( N_2. \) (b) Experimental results on logarithmic pressure scale. The inset in the lower panel is a magnification of the sample’s initial contraction at low relative pressure.

Figure 4. Results of the \textit{in situ} dilatometry measurement for adsorption of (a) \( CO_2 \) (273 K) and (b) \( H_2O \) (298 K) on the carbon sample. Upper panels: sorption isotherm; lower panels: corresponding strain isotherm. Full symbols denote adsorption and open symbols desorption. The insets in the lower panels are magnifications of the sample’s contraction at low relative pressure. In (a) the relative pressure is given on a logarithmic scale.
Because of the experimental temperature of 273 K, micropore filling with CO₂ (see Figure 4a) takes place in a significantly higher relative pressure range than for N₂ and Ar at 77 K. Also, the initial contraction observed for CO₂ is smaller by a factor of approximately 2 to 3 compared to N₂ or Ar, respectively. To some extent this difference between the strain isotherms of N₂/Ar and CO₂ can be attributed to sample temperature during the CO₂ experiment, since it was shown that with increasing temperature the effect of initial contraction during micropore filling becomes less pronounced. Thus, for CO₂ adsorption at lower temperatures we would expect the initial contraction to become quantitatively more comparable to the N₂ and Ar results. An analogue comparison between the maximal expansions of CO₂ and N₂/Ar deformation data is not possible because of the experimental relative pressure limit of 0.03 in the case of CO₂. As anticipated, within the accuracy of the experimental techniques applied, both the CO₂ adsorption and related strain isotherm are found to be fully reversible without any evidence of hysteresis effects.

The adsorption of H₂O in carbons is fundamentally different from the adsorption of the other adsorbates investigated because of the weak interaction energy of the polar H₂O molecules with a typically nonpolar carbon surface. An overview on the topic of H₂O adsorption in carbons can be found e.g. in ref. 70. According to ref 71 the adsorption of H₂O molecules is initiated on surface functional groups forming clusters of several molecules, which eventually grow and coalesce filling the micropores. This is also reflected by the high relative pressure range of H₂O adsorption for the sample investigated (see Figure 4b). It should be noted that the exceptional adsorption mechanism of H₂O on carbon also hampers capillary condensation in mesopores, which was experimentally only reported for pore sizes significantly below 10 nm (see e.g. ref 72). Therefore, H₂O filling of the mesopores present in our sample is not possible (see pore size distribution in Figure 2a), though the slight increase in H₂O adsorption for relative pressure above 0.9 may correspond to the onset of capillary condensation. Furthermore, the H₂O adsorption and strain isotherms in Figure 4b show clear hystereses; i.e., both desorption branches are shifted to lower relative pressures compared to the respective adsorption branches. The hysteresis of H₂O adsorption isotherms for carbons is a well-known phenomenon (see e.g. ref 38), which was recently interpreted as kinetically forbidden transformations between different metastable configurations of H₂O molecules within carbon micropores. A hysteresis loop corresponding to the H₂O adsorption process is also found in the strain isotherm. The adsorption branch of the H₂O strain isotherm exhibits a slightly deeper minimum than the desorption branch, but otherwise the shift in p/p₀ between both deformation branches appears to result from the adsorption hysteresis. Earlier studies on coals found significant hysteresis effects in dilatometric measurements on coals for the adsorption/desorption of H₂O, however, only in combination with broad adsorption hysteresis loops. On the other hand, microporous coals without a H₂O adsorption hysteresis also exhibited no deformational hysteresis, leading to the conclusion that the two hysteresis loops are generally correlated. A quantitative comparison of the H₂O strain isotherm with the other adsorbates reveals that for H₂O the initial contraction is more pronounced than for any of the other adsorbates, i.e., a factor of 2 compared to Ar, a factor of 3 compared to N₂, and a factor of 6 compared to CO₂ (see Figure 5). Contrarily, the expansion close to saturation pressure is found at a relative length change of approximately 0.09% in the H₂O experiment, while for N₂ and Ar the sample expands up to 0.35%, corresponding to nearly 4 times the maximum expansion observed for H₂O. However, as can be seen from Figures 5b and 5c, the differences in maximal expansion between H₂O and N₂/Ar are less pronounced, if we limit our analysis to the region of micropore filling. Noteworthy in ref 39 the comparison of strain isotherms of a coal rod for the adsorption of N₂, Ar, and H₂O at 25 °C showed the reverse trend; i.e., the adsorption of N₂ and Ar caused less expansion than the adsorption of H₂O. This apparent discrepancy to our results can be explained by the above-mentioned temperature dependence of adsorption-induced deformation: While the H₂O experiments in this work and in ref 39 were performed at the same temperature of 25 °C, the temperature of the N₂ and Ar experiments here and in ref 39 differs by over 200 K (77 K here and 25 °C in ref 39). Consequently, for our N₂ and Ar measurements at 77 K sorption-induced expansion is significantly more pronounced than in ref 39 and thus larger than the observed deformation for H₂O adsorption at 25 °C.

An obvious question to be addressed is whether all adsorbates applied can access the entire micropore volume present in our sample. From the comparison of the carbon density pₖ derived from N₂ adsorption, He pycnometry, and DGE data we concluded this to be true for the N₂ molecule. Considering the kinetic molecular diameter dₖₐₒˡ of the adsorbates (see Table 2), we find Ar and CO₂ to be very similar but slightly smaller in size than N₂. Also, the micropore size distributions derived from N₂, Ar, and CO₂ NLDF analysis show very similar cumulative micropore volume at the upper end of the micropore size range (Figure 2b). Therefore, Ar and CO₂ should not exhibit any steric restrictions to microporosity either. For H₂O matters are more complicated. While the kinetic diameter of single H₂O molecule is significantly smaller than the other adsorbates applied, the size of an adsorbed H₂O cluster, which may be more relevant and was estimated by small-angle X-ray scattering to be about...
0.4 nm in diameter,74 is larger than a N2 molecule. With respect to the micropore size distribution we derived for our sample by CO2 NLDFT analysis (Figure 2b), H2O clusters could therefore exhibit steric restriction to micropores in the range of 0.35–0.4 nm, which would exclude up to 20% of the micropore volume present in the sample from H2O filling. To cross-check the potential steric restriction for H2O to the sample’s microporosity, we calculated the density of the adsorbed H2O ($\rho_{\text{ads}}(\text{H}_2\text{O}) = 0.78$ g/cm$^3$) from the respective adsorption isotherm assuming the micropore volume $V_{\text{mic}}$ to be filled at a relative H2O pressure of $p/p_0 = 0.9$. The same approach was reported for a micro- and mesoporous CMK-3 carbon sample, yielding a density for the adsorbed water of 0.81 g/cm$^3$, which in turn is in good agreement with other values found for the H2O density within carbon micropores, e.g., ref 75. However, in contrast to the sample investigated in this paper, CMK-3 can be entirely filled during H2O adsorption due to its small mesopore size, and consequently in CMK-3 the volume of pores smaller than 0.4 nm is negligible compared to the overall H2O filled pore volume. Thus, given the good agreement between the adsorbed water densities derived for both carbons, we conclude that the entire micropore volume of our sample was filled with H2O, since otherwise the H2O density calculated for our sample should be significantly lower than for CMK-3.

Another way to quantitatively compare the deformation induced by adsorption of N2, Ar, CO2, and H2O is a plot of the measured strains versus the respective amount adsorbed. In Figure 5a, this is done for the amount adsorbed in specific molar quantity revealing a further trend: in parallel to the previously described variation of the maximum contraction (i.e., for CO2 the contraction is least pronounced becoming systemically more distinct for N2, Ar and H2O), there is the same systematic variation with respect to the amount adsorbed at the minimum of the strain isotherm. In particular, the amount adsorbed at the deformation minimum is approximately 10 times higher for H2O than for CO2. Analogous plots with the amount adsorbed converted into liquid volume (using the free liquid density) and adsorbate volume are shown in Figures 5b and 5c, respectively. The densities of adsorbed N2, Ar, and CO2 were derived from NLDFT calculations reported in ref 65; i.e., we took the average molar volume $V_{\text{mol}}$ of the respective adsorbate over the pore width range present in our sample (3.5–8 Å, compare Figure 3) at saturation pressure and calculated the adsorbate density $\rho_{\text{ads}}$. For H2O the above given density $\rho_{\text{ads}}(\text{H}_2\text{O}) = 0.78$ g/cm$^3$ was used. Free liquid and predicted adsorbate densities of the adsorbates employed are given in Table 2. Figures 5b and 5c prove that the observed deformations are not directly related to the relative volumetric filling of the microporosity. Also, the similarity between the mechanisms of adsorption of N2 and Ar is clearly shown, while mechanisms of adsorption of CO2 and especially H2O are significantly different.

As noted in the Introduction, theoretical studies predicted the packing, i.e., the spatial arrangement of the adsorbed molecules inside a micropore, to be the key parameter determining the solvation pressure and therefore the pore deformation. The adsorbate packing inside the micropore at thermodynamic equilibrium (constant temperature and pressure) in turn results from the competition between the long-range attraction of the adsorbate–adsorbent interaction and the short-range repulsion between molecules. Additionally, there is a geometrical/sterical boundary condition defined by the ratio of the adsorbate molecular size and the micropore width. If the arrangement of the adsorbed molecules within the micropore becomes ordered and dense, an expansion of the micropore is energetically favorable, since it counterbalances the short-range repulsion between solid and fluid molecules. Contrarily, below a certain density of the adsorbed molecules the mediation of the long-range attractive wall potentials by the adsorbed fluid will be dominant over the short-range repulsion, thus causing the pore to contract. In short, the adsorbate always deforms the pore to minimize the overall free energy of the pore–adsorbate system. In order to compare this theoretical concept with our experimental results, a criterion for the packing of the adsorbed molecules is required. Here we chose the ratio of the adsorbed phase density at saturation pressure and the respective free liquid density $p_l = \rho_{\text{ads}}/\rho_{\text{liquid}}$ (see Table 2), which describes whether the given adsorbate is more or less densely packed inside the micropores than it would be under unconfined conditions. For N2 and Ar we find $p_l$ less than 5% higher than unity, indicating only moderate impact of the micropore confinement on the molecular packing of N2 and Ar, while for CO2 $p_l$ is significantly larger than 1; i.e., adsorbed CO2 is significantly denser packed inside the micropore than in free liquid state. Hence, we expect stronger contributions from the short-range repulsion of the CO2–CO2 and CO2–carbon interactions and increased expansion of the micropores. This fits our observation that for a given amount adsorbed the adsorption of CO2 causes less contraction or more expansion, respectively, than for N2 and Ar adsorption (compare Figure 5c). Contrarily, the density of adsorbed H2O molecules is lower than in the free liquid ($p_l(\text{H}_2\text{O}) < 1$), and thus the attractive interactions between solid and fluid molecules should become more pronounced, resulting in overall enhanced contraction compared to any other of the adsorbates applied. Again, this expectation is met by our experiment. Therefore, we conclude that the differences of adsorption-induced deformation observed for N2 (77 K), Ar (77 K), CO2 (273 K), and H2O (298 K) correlate indeed with the variations of the molecular packing of the adsorbed molecules compared to their free liquid state.

4. CONCLUSIONS

We presented experimental data for adsorption-induced deformation in a synthetic microporous carbon obtained by in situ dilatometry for the adsorbates N2 (77 K), Ar (77 K), CO2 (273 K), and H2O (298 K). The shape of the strain isotherms was found to be qualitatively similar for all adsorbates, i.e., contraction for initial stages of micropore filling followed by a transition to expansion for proceeding adsorption. Comparing the densities of the adsorbates inside carbon micropores to their free liquid state, we found support for the theoretically predicted correlation between adsorption-induced deformation and molecular packing: N2 and Ar both exhibit similar densities in free liquid and adsorbed state, and their adsorption-induced deformation is comparable. In contrast, CO2 is significantly compacted inside the carbon micropore, enhancing the positive solvation pressure resulting from the short-range repulsive fluid–fluid and solid–fluid interactions. H2O molecules, on the other hand, pack less densely inside carbon micropores than the respective free liquid, and consequently the short-range repulsive interactions are reduced and the mediation of the attractive wall potentials becomes more apparent.
The experimental data presented here provide a better qualitative understanding of the role of adsorbate packing on adsorption-induced deformation in micropores that may help develop advanced experimentally informed theoretical models for quantitative description of adsorption on compliant microporous solids. To the best of our knowledge, we for the first time demonstrated with the N₂ strain isotherm the existence of two nonmonotonic stages of subsequent contraction and expansion in the regions of micro- and mesopore filling. This characteristic behavior is expected for any material with a micro-mesoporous structure.

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**Notes**

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